

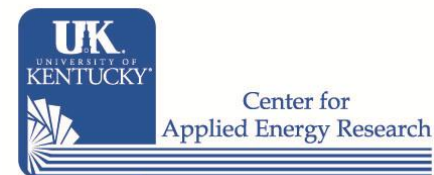
Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Ultrasonics

DE-FE0007741

Budget Period 1

NETL Project Review

October 9, 2012



Principal Investigator
Sonja Salmon
sisa@novozymes.com

Notices

- **ACKNOWLEDGEMENT OF GOVERNMENT SUPPORT.** This material is based upon work supported by the Department of Energy under Award Number DE-FE0007741.
- **DISCLAIMER.** This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
- **COPYRIGHT NOTICE.** Copyright, 2012, Novozymes North America, Inc., Pacific Northwest National Laboratory, University of Kentucky Research Foundation, and Doosan Power Systems Ltd.

The use in this report of any copyrighted data owned by any of the above parties is authorized pursuant to the relevant contract between such party and Novozymes North America, Inc., relating to the Department of Energy Award Number DE-FE0007741. For such copyrighted data, the copyright owner has granted to the Government, and others acting on its behalf, a paid-up, nonexclusive, irrevocable, worldwide license to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government, for all such data

Agenda



- Project Overview
 - Main Messages
 - Partners, Budget & Schedule
 - Overall Project Objective & Concept
- Key BP1 Accomplishments
 - Laboratory Validations
 - Preliminary Feasibility Study
- Plans for Bench-scale Evaluation
 - Bench-scale Design
 - Bench-scale Test Matrix

Main Messages

Key Findings

- Within the boundaries of the pre-feasibility framework, the concept will provide 25% reduction in LCOE versus Case 10, with a potential to reduce to 51%
- An integrated design for bench-scale has been established
- Lab results support moving to bench-scale testing

Path Forward

- Project team recommends proceeding to BP2
- Technical gaps identified in BP1 that are important for bench-scale testing are incorporated in the go-forward plan
- Certain technical and commercial aspects will need to be addressed outside the scope of this project

Project Overview

- DOE Project Manager: Andrew Jones
- Project Participants



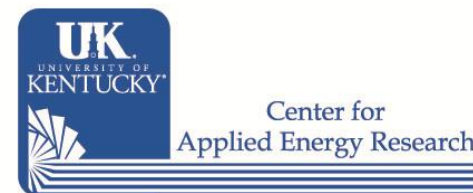
Ultrasonics & Aspen®



Full Process Analysis



Enzymes & Solvents



Kinetics & Bench-scale Tests

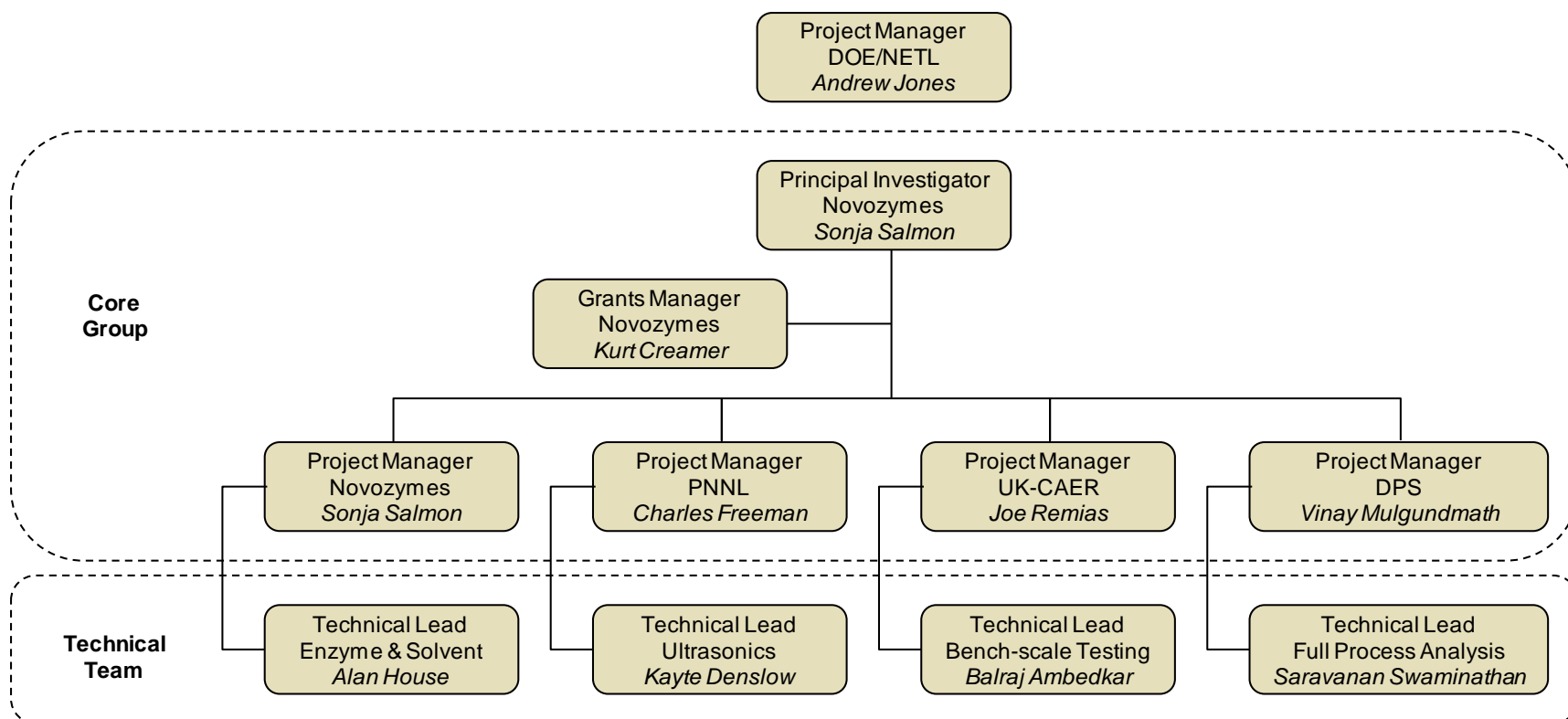
- Project Duration: Oct. 1, 2011 – Dec. 31, 2014
- Total Project Budget: \$2,088,643
 - FFRDC Share: \$489,949
- Total Project Award: \$1,598,694
 - DOE Share: \$1,168,670
 - Total in-kind Cost Share: \$430,024

DOE Program Objectives

Develop solvent-based, post-combustion technology that

- Can achieve $\geq 90\%$ CO₂ removal from coal-fired power plants
- Demonstrates progress toward the DOE target of <35% increase in LCOE.

Project Management Team



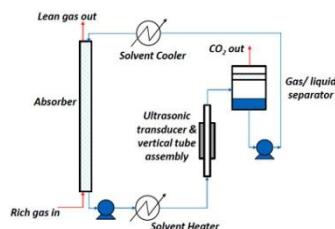
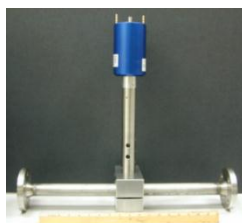
Project Schedule

- Task 1 – Project Management and Planning
- Task 2 – Process optimization
 - Ultrasonic Unit Optimization
 - Solvent & Enzyme-Solvent Compatibility Optimization
 - Solvent Physical Properties & Kinetic Measurements
 - Design Integrated Bench-Scale System
- Task 3 – Initial Technical & Economic Feasibility
- Task 4 – Bench Unit Procurement & Fabrication
- Task 5 – Unit Operations Shakedown Testing & Integration
- Task 6 – Bench-scale Testing
- Task 7 – Full Technology Assessment



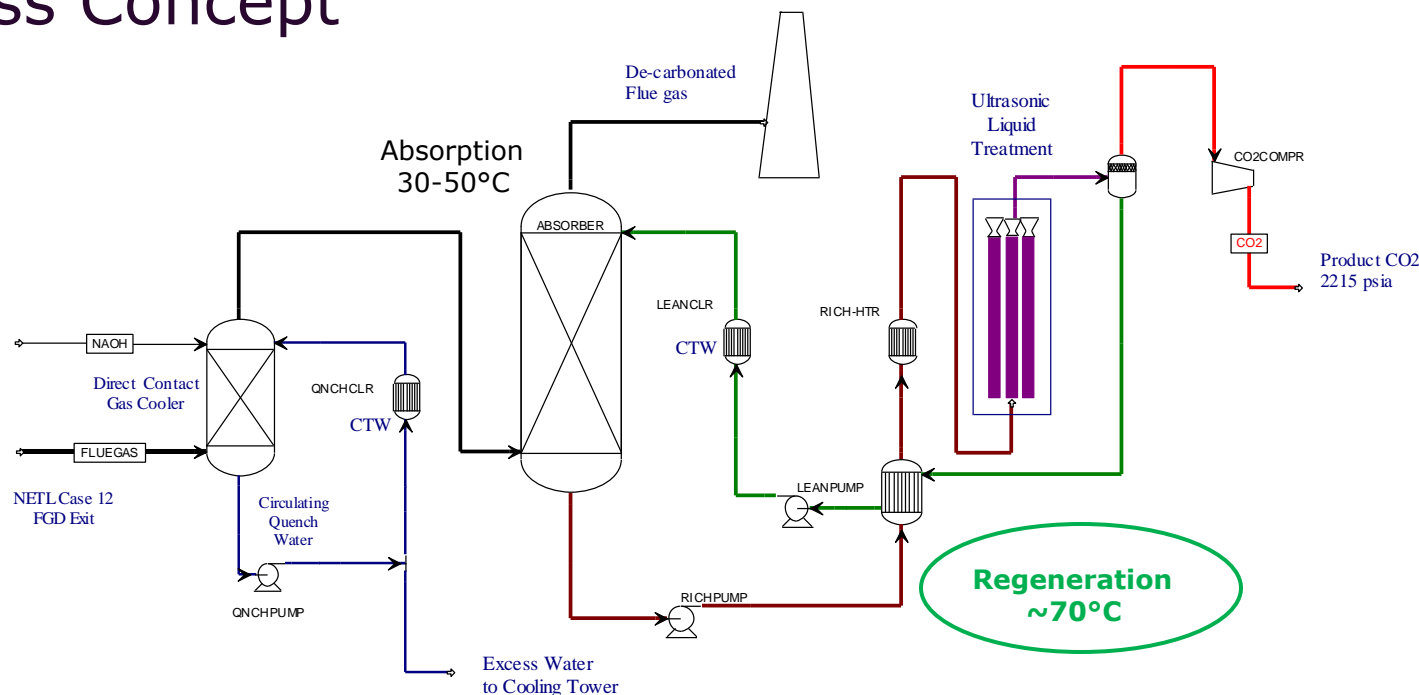
Overall Project Objective

Complete a *bench-scale study* and corresponding full technology assessment to validate the potential in meeting the DOE Program Objectives of a *solvent-based post-combustion carbon dioxide capture* system that integrates



- a low-enthalpy, aqueous potassium carbonate-based solvent
- with an absorption-enhancing carbonic anhydrase enzyme catalyst
- and a flow through ultrasonic-enhanced regenerator
- in a re-circulating absorption-desorption process configuration

Process Concept



Advantages

- Low enthalpy, benign solvent (catalyzed aq. 20% K₂CO₃)
 - K₂CO₃ ΔH_{rxn} 27 kJ/mol CO₂
 - MEA ΔH_{rxn} 83 kJ/mol CO₂
- Potential for ~50% regeneration energy vs. MEA

Challenges

- Demonstrate atmospheric regeneration at 70°C enabled by ultrasonics
- Demonstrate overall techno-economic feasibility
 - energy demand
 - enzyme requirement

Budget Period 1 Milestone Status

ID	Milestone Description	Completion Date	Success Criteria	Performance Level Achieved
N1	Submit Project Management Plan	11/10/2011	DOE approval	Approved and on file
N2	Conduct Kick-off Meeting	11/8/2011	Completion	Presentation posted on NETL project site
P1	Determine optimal ultrasonic regenerator operating conditions	8/31/2012	Ultrasonics achieves lean loading equivalent to vacuum stripping at 70°C	Achieved 30% of CO ₂ desorption working range target
N3	Down-select to the optimal enzyme-solvent formulation	8/31/2012	Select a base-case recipe for use in prefeasibility study	Selected 20 wt% K ₂ CO ₃ with 3g/L enzyme and defined lean/rich range
N4	Updated solvent State Point Data Table	8/31/2012	Submission to DOE	Provided in Supplementary Milestone Briefing
K1	Complete kinetic measurements of optimal enzyme-solvent in WWC	8/31/2012	Enzyme-solvent kinetics are ≥ 50% versus 30 wt% MEA under same process conditions	Milestone mass transfer achieved
N5	Complete detailed bench-scale unit design	10/4/2012	Submission to DOE	Design integration of all process elements was achieved
D1	Complete Preliminary Technical and Economic Feasibility Study	10/1/2012	Submission to DOE	Project Team recommendation to proceed to BP2

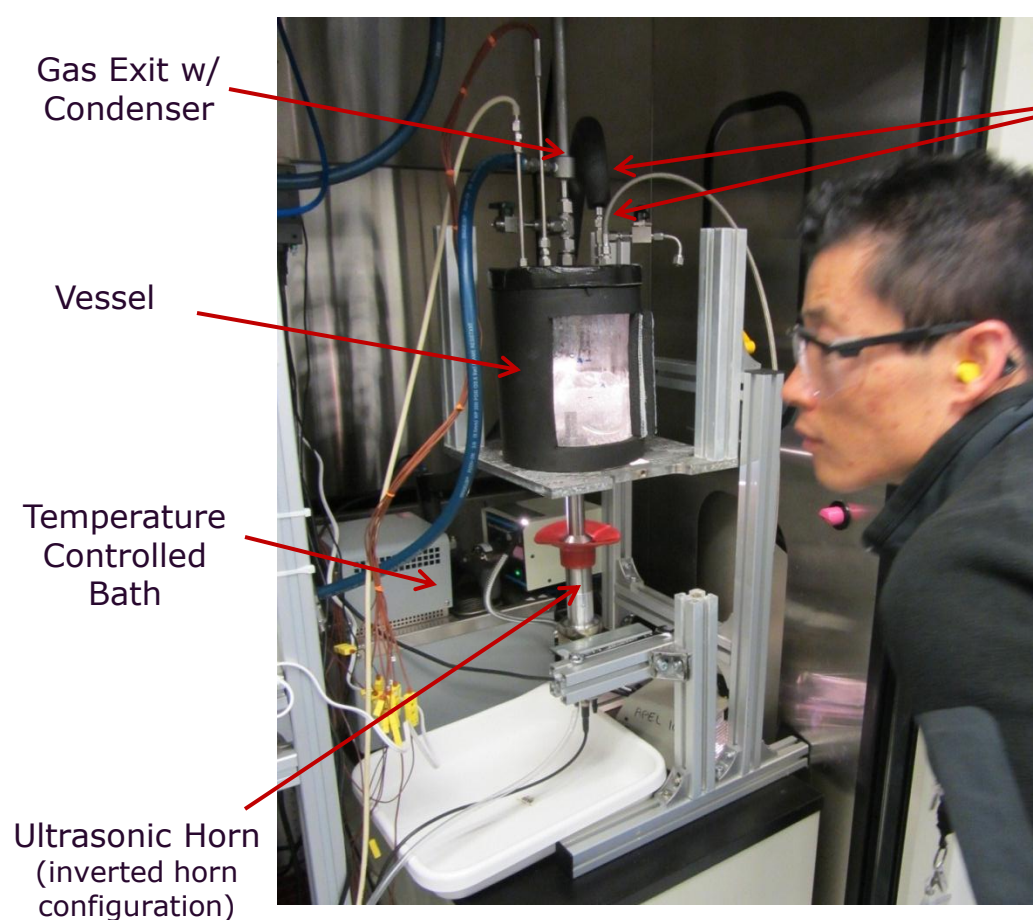
Key BP1 Accomplishments: Laboratory Validations

- Ultrasonic Unit Optimization
 - Demonstrated CO₂ release via ultrasonic energy addition
 - 1/3rd of target defined by ASPEN®-predicted vacuum
 - Established preliminary settings for ultrasonic power, frequency, and exposure times.
 - Established need for continuous bubble removal
- Solvent & Enzyme-Solvent Compatibility Optimization
 - Lab results show robustness to simulated process pH, ultrasonics, and absorber temp. with (manageable) losses at increased temp.
 - Suitable antifoam identified if required
- Solvent Physical Properties & Kinetic Measurements
 - Milestone mass transfer achieved
 - 40 °C absorption temperature maximizes mass transfer
 - Initial enzyme loading for process established
 - State Point Data Table presents solvent physical properties

Ultrasonic Unit Optimization

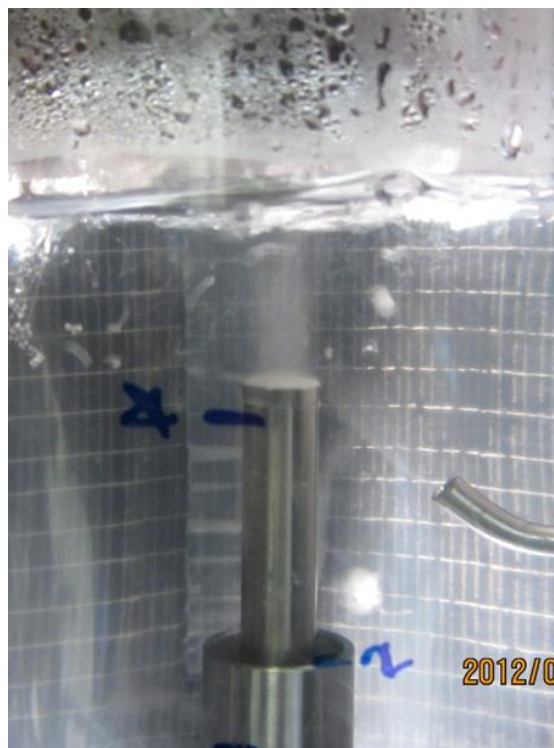


PNNL's Batch Lab Ultrasonic Desorption System

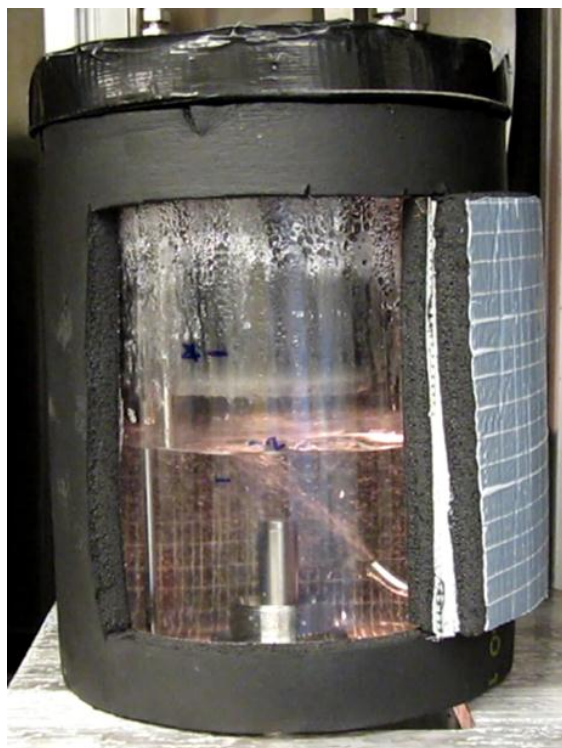


- Bubbles expand and shrink in an ultrasonic field
 - Expanding bubbles = lower pressure/ higher surface area
 - Shrinking bubbles = higher pressure/ lower surface area
- Rectified diffusion results when expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution
 - Frequency optimization likely required for optimal bubble growth
- Remove bubbles before they can dissolve back into the liquid

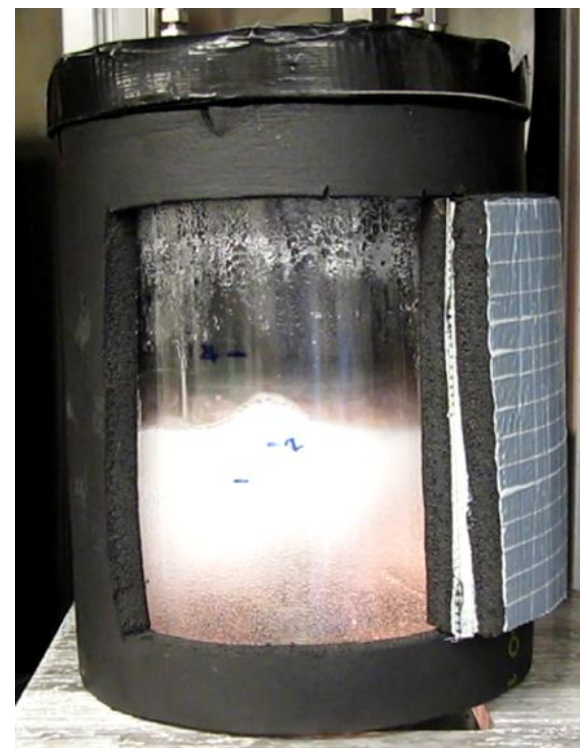
Photographs of Ultrasonic Desorption



*Pure Water at 70°C
– With Sonication*



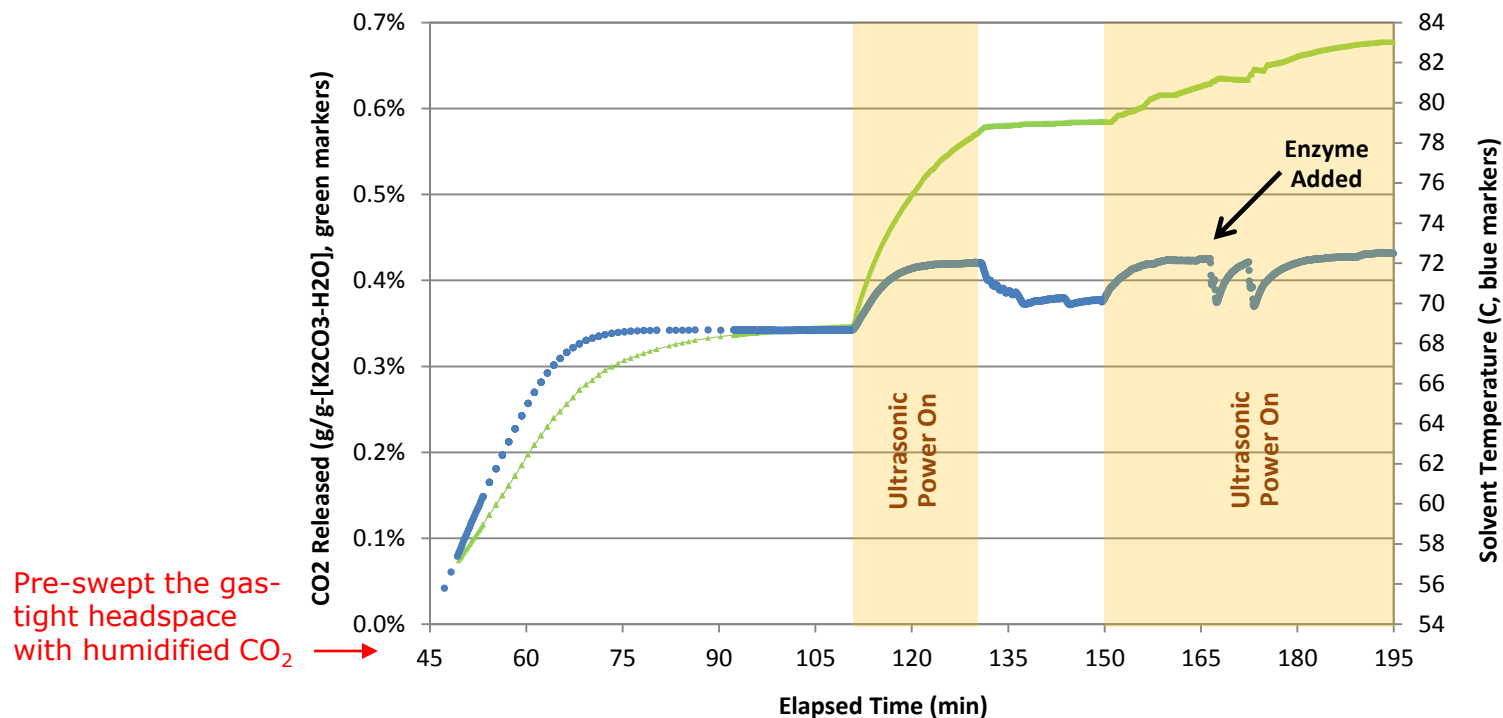
*Loaded Solvent at 70°C
– No Sonication*



*Loaded Solvent at 70°C
– With Sonication*

Significant agitation/ bubbling observed when ultrasonic power added to CO₂ loaded 20% K₂CO₃ solution at 70°C

Batch Test Results for Ultrasonic Regeneration



- ▶ Testing with 20 wt% K₂CO₃ solvent loaded to 4.6 wt% CO₂
- ▶ ASPEN (equilibrium) projections of CO₂ release at 6 psia = 0.96%
- ▶ Total CO₂ release observed = 0.67% (0.25% from ultrasonic effect) – likely impacted by re-dissolution of CO₂
- ▶ Slow CO₂ release rates observed – also likely impacted by re-dissolution of CO₂

Energy Projections for Ultrasonic Regeneration

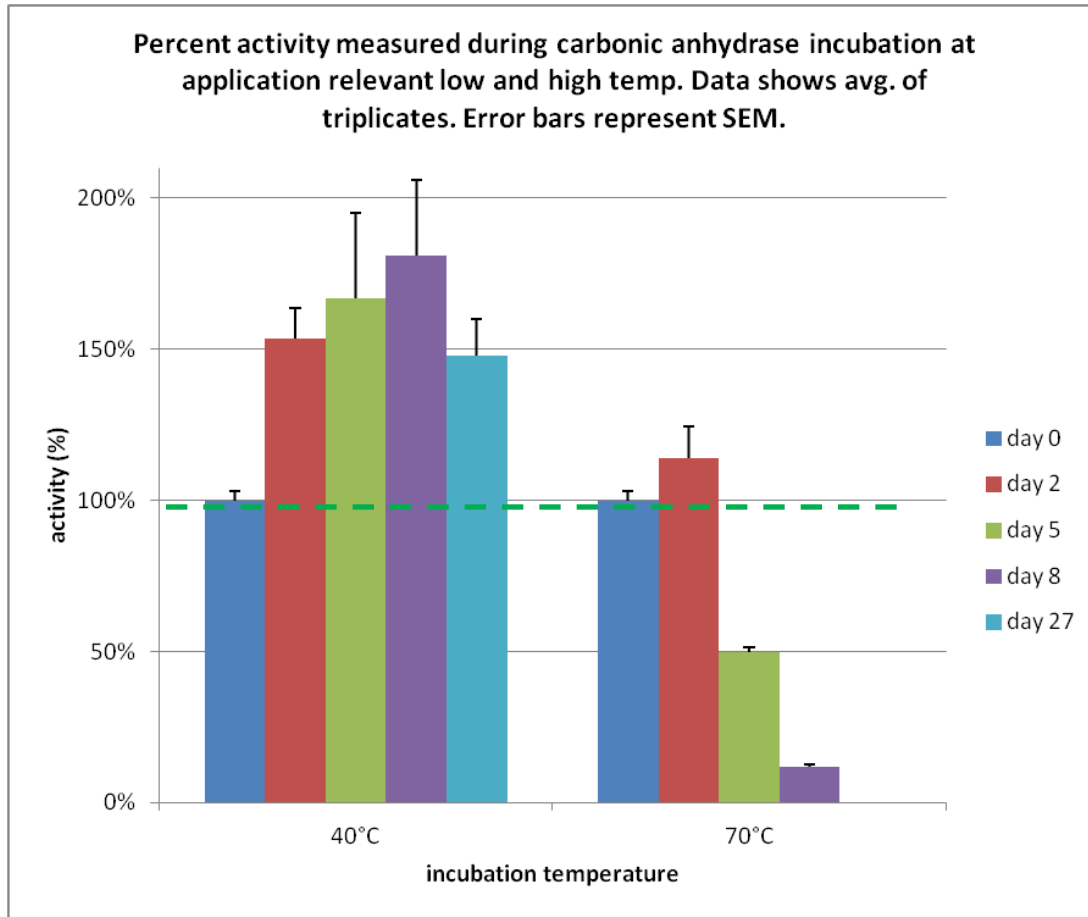
- ▶ Commercial water sterilization = 0.24 to 0.79 kJe/ kg of water
 - Based on developed applications for ship ballast treatment [1]
- ▶ Initial batch testing for CO₂ regeneration = 4.9 kJe/ kg of solvent
 - Laboratory horn used. Poor CO₂ removal (significant re-dissolution)
 - Demonstrated value = 10.3 kJe /mol of CO₂, 0.021 kg of CO₂ removal per kg of recirculated solvent recirculation assumed.
- ▶ Full-scale CO₂ regeneration system estimate = 1.5 kJe/ kg of solvent
 - Based on (conservative) tube sonication configuration
 - Equates to just over 11 MWe of parasitic power for the ultrasonic system in the 500 MWe reference system)

[1] "Ballast water treatment technology, Current status," February 2010
(http://www.lr.org/Images/BWT0210_tcm155-175072.pdf)

Enzyme-Solvent Compatibility



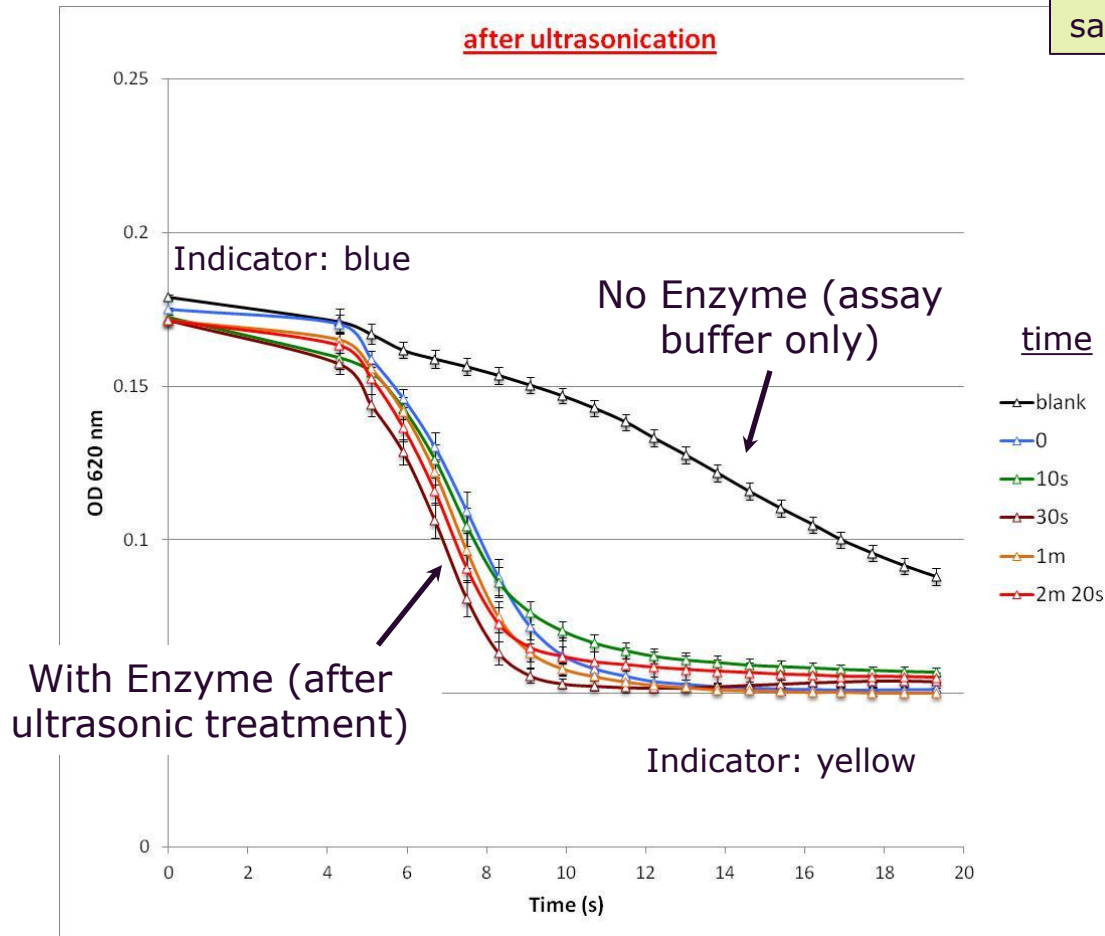
Enzyme-solvent Compatibility



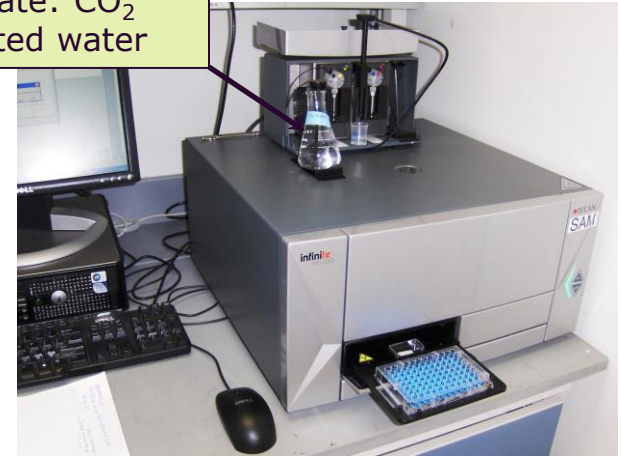
- Demonstrates high robustness in working solvent at 40°C
- Demonstrates limited (but nevertheless useful) robustness at 70°C
- Data used for initial estimation of solvent replenishment rate in prefeasibility

Solvent: aq. 22% $K_2CO_3/KHCO_3$ with 3 g/L enzyme and adjusted to lean pH

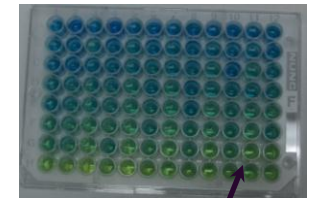
Enzyme Compatibility with Ultrasonic Treatment



Substrate: CO₂ saturated water



Indicator color changes due to pH decrease when CO₂ is hydrated to bicarbonate

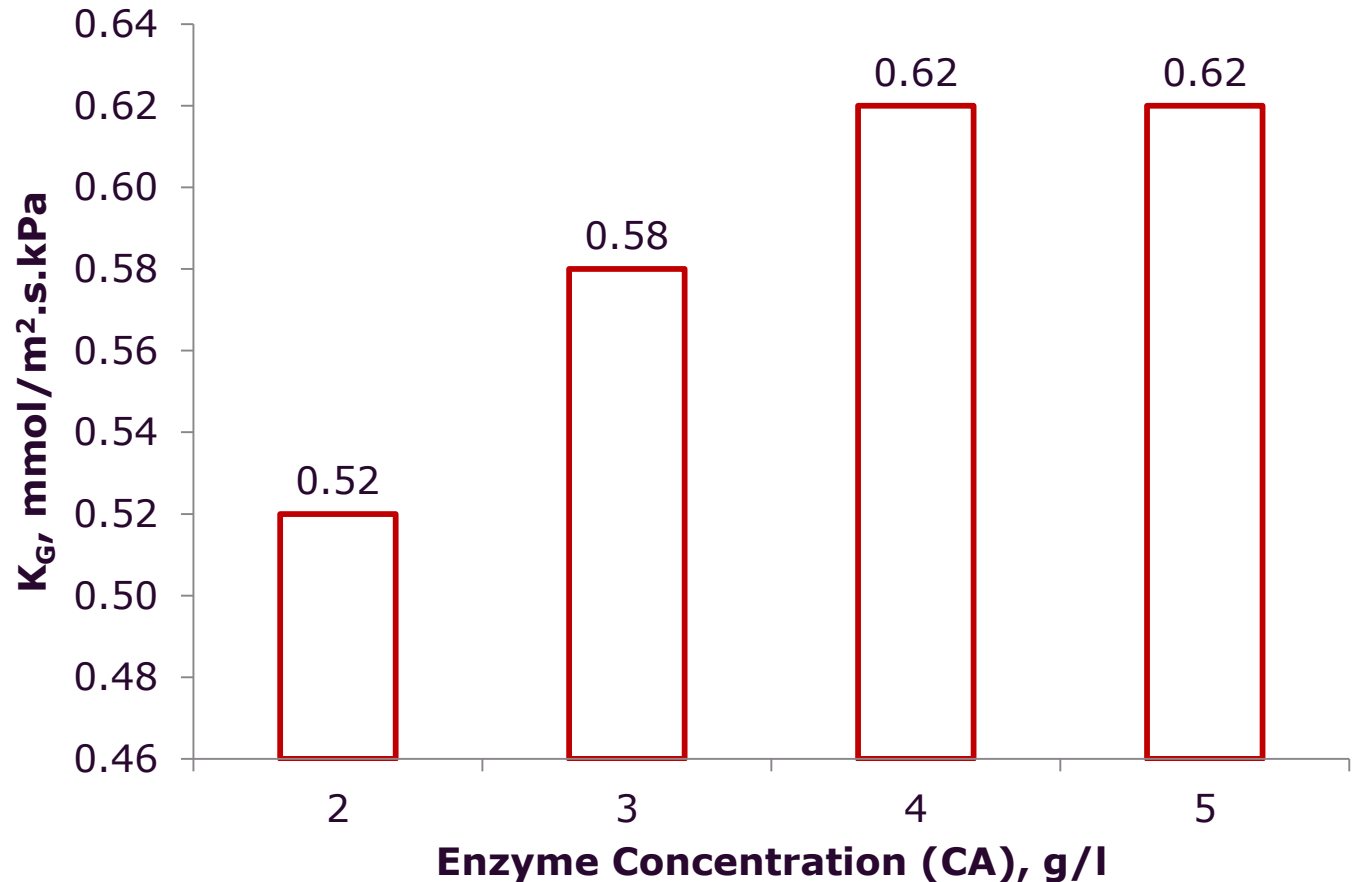


- **Enzyme tolerates initial ultrasonic tests** with no apparent loss of activity
- **Automated enzyme assay was developed** for use throughout the project

Solvent Kinetic Measurements

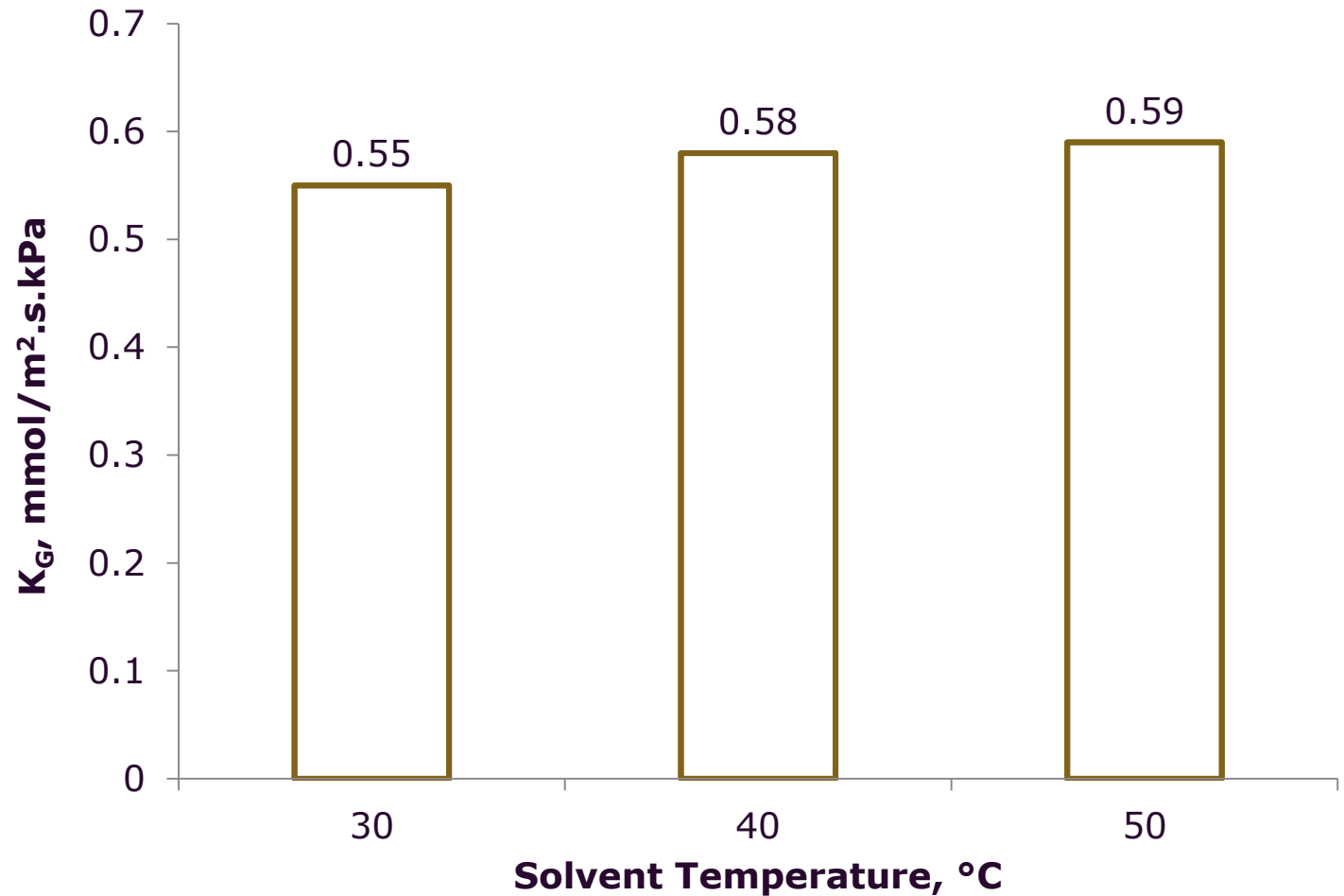


UK-CAER Mass Transfer Results



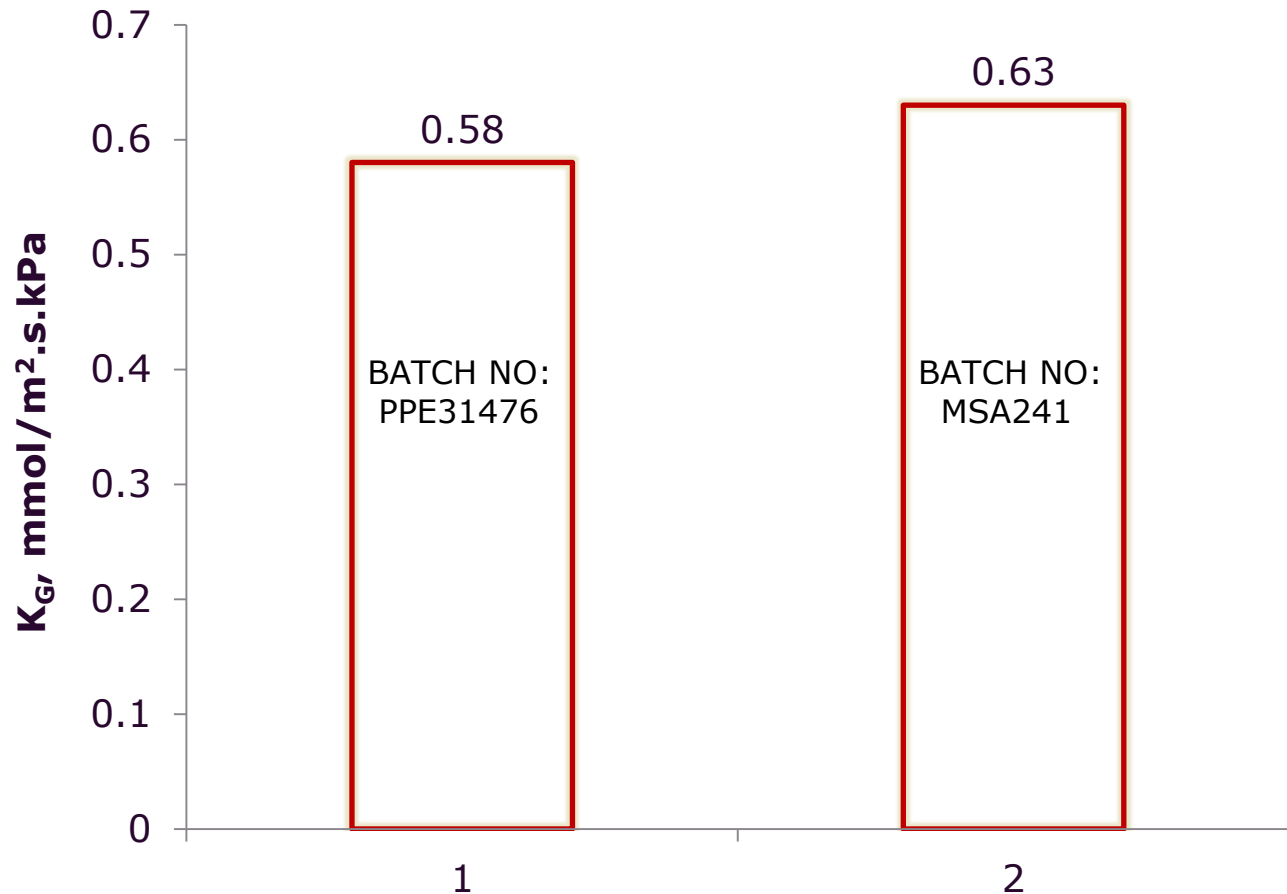
- Solvent: aq. 20% K₂CO₃ + carbonic anhydrase
- **Achieved Initial Milestone Enzyme-catalyzed Solvent Kinetics (Mass Transfer)**

UK-CAER Mass Transfer Results



- Solvent: aq. 20% K_2CO_3 + carbonic anhydrase

UK-CAER Mass Transfer Results



- Solvent: aq. 20% K_2CO_3 + 3 g/L carbonic anhydrase
- **Achieved Initial Milestone Enzyme-catalyzed Solvent Kinetics (Mass Transfer)**

Preliminary Technical & Economic Feasibility



Preliminary Technical and Economic Feasibility

- Overall CO₂ Capture Reaction

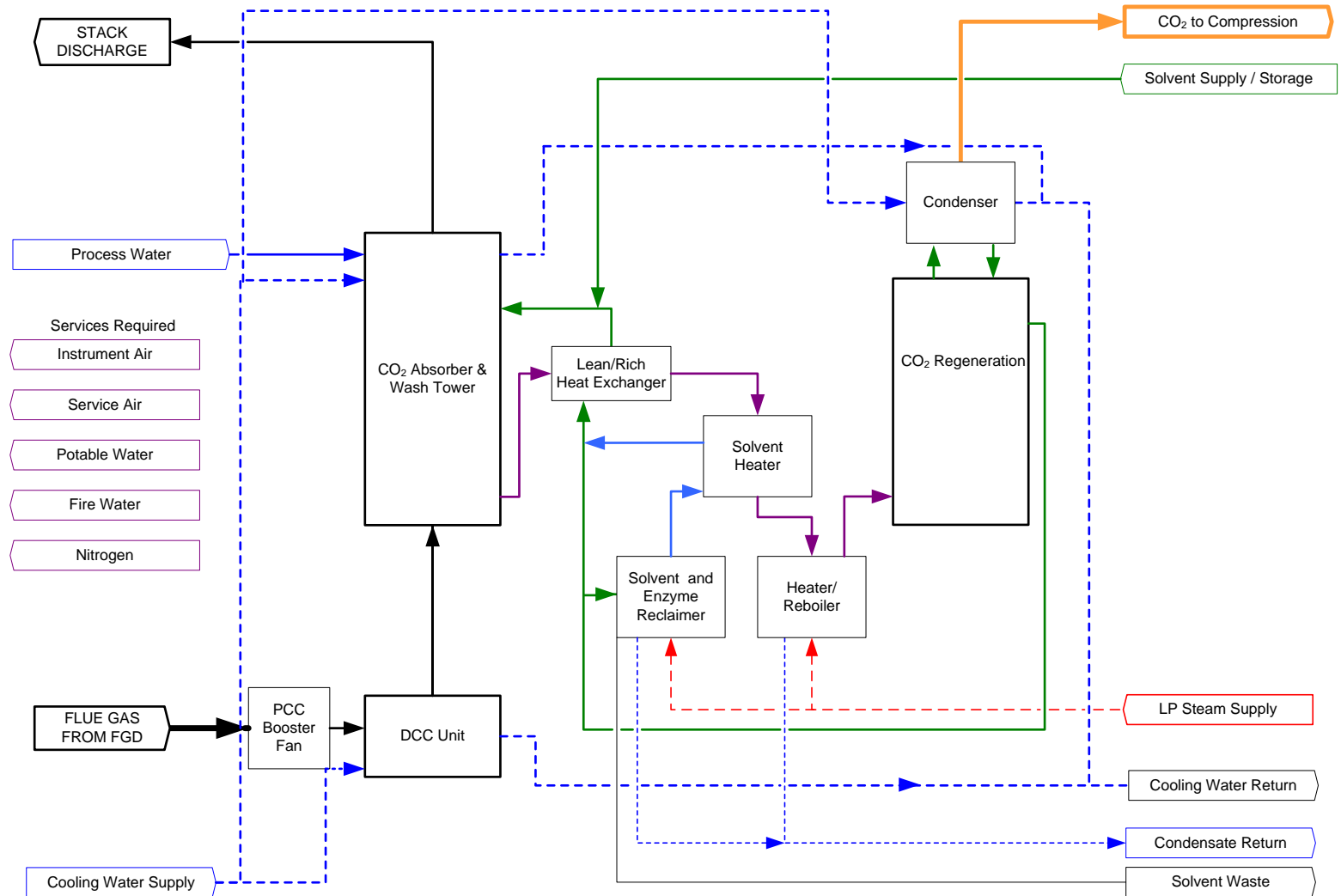


- Aspen Plus® (with Radfrac) used for Process modeling for absorption
- AspenTech's Capital Cost Estimator® along with budget supplier quotations used for Cost Estimation of the PCC Components
- Preliminary techno-economic feasibility and sensitivity studies performed based on the fixed coal feed rate as per Case 10 for the enzyme enhanced K₂CO₃ solvent.
- Four methodologies of regeneration have been investigated:
 - Case 1: Vacuum Stripping using the LP steam
 - Case 2: Optimized Vacuum Stripping using VLP steam at 8psia
 - Case 3: Ultrasonic regeneration by the LP steam
 - Case 4: Optimized Ultrasonic regeneration using VLP steam at 8psia

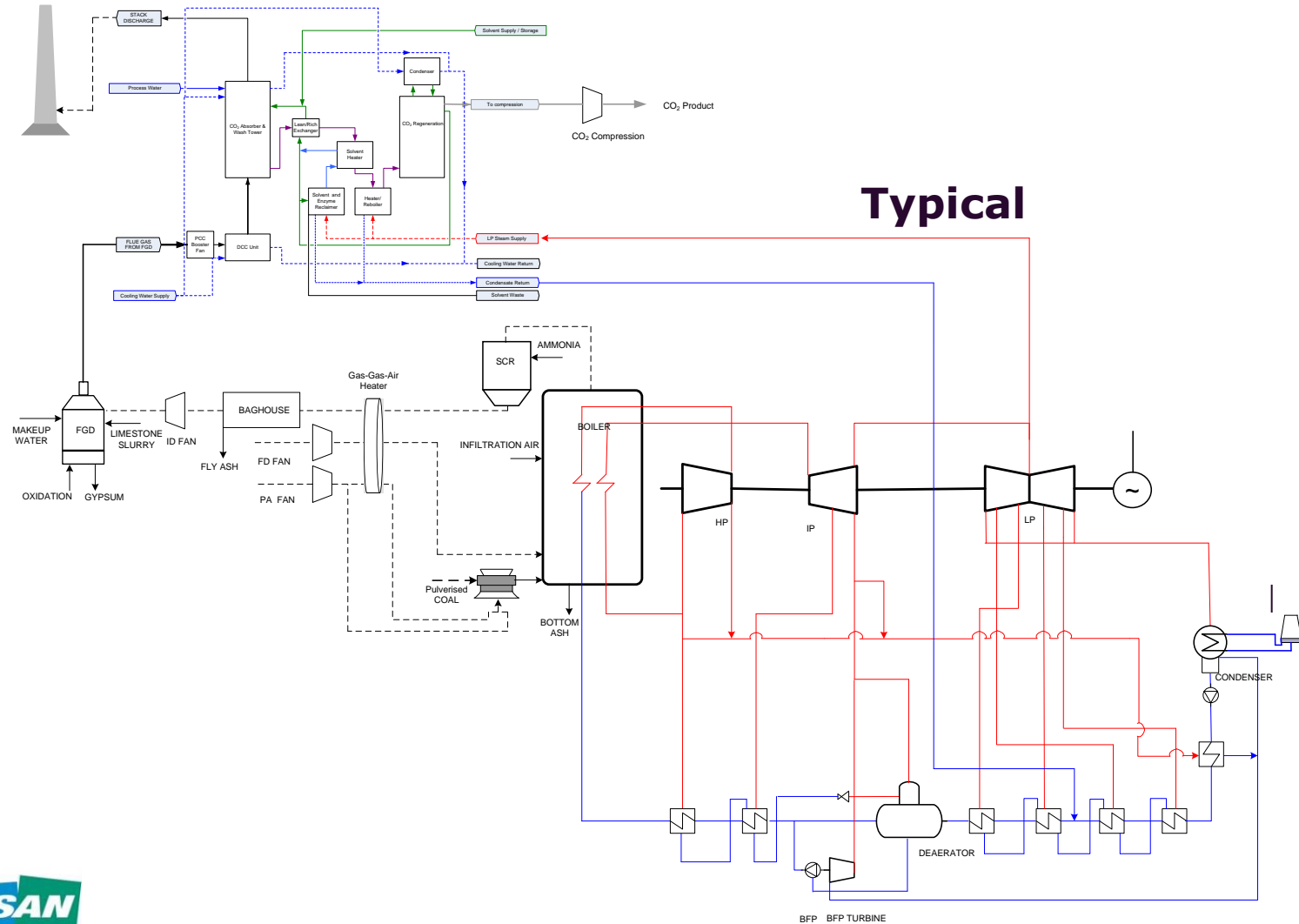
Evaluation Basis and Assumptions

- The Econamine FG+ block in Case 10 of the 2007 DOE/NETL Study was replaced with the novel PCC process.
 - Flue gas inlet from the FGD, CO₂ product gas to compression and off-gas emissions set as system boundaries
- The amount of LP steam not used (compared with Case 10) has been returned to the LP turbine for power generation.
- Enzyme loading, makeup rate and costs were selected based on experimental data and Novozymes' historical internal knowledge.
- FGD polisher has not been considered as part of this assessment because the enzyme is not susceptible to acid gas degradation at the SO_x and NO_x levels encountered.
- Techniques for removal of HSS will be investigated in the next phase of the project.
- An enzyme reclamation methodology has been considered due to enzyme's degradation by exposure to high temperatures.

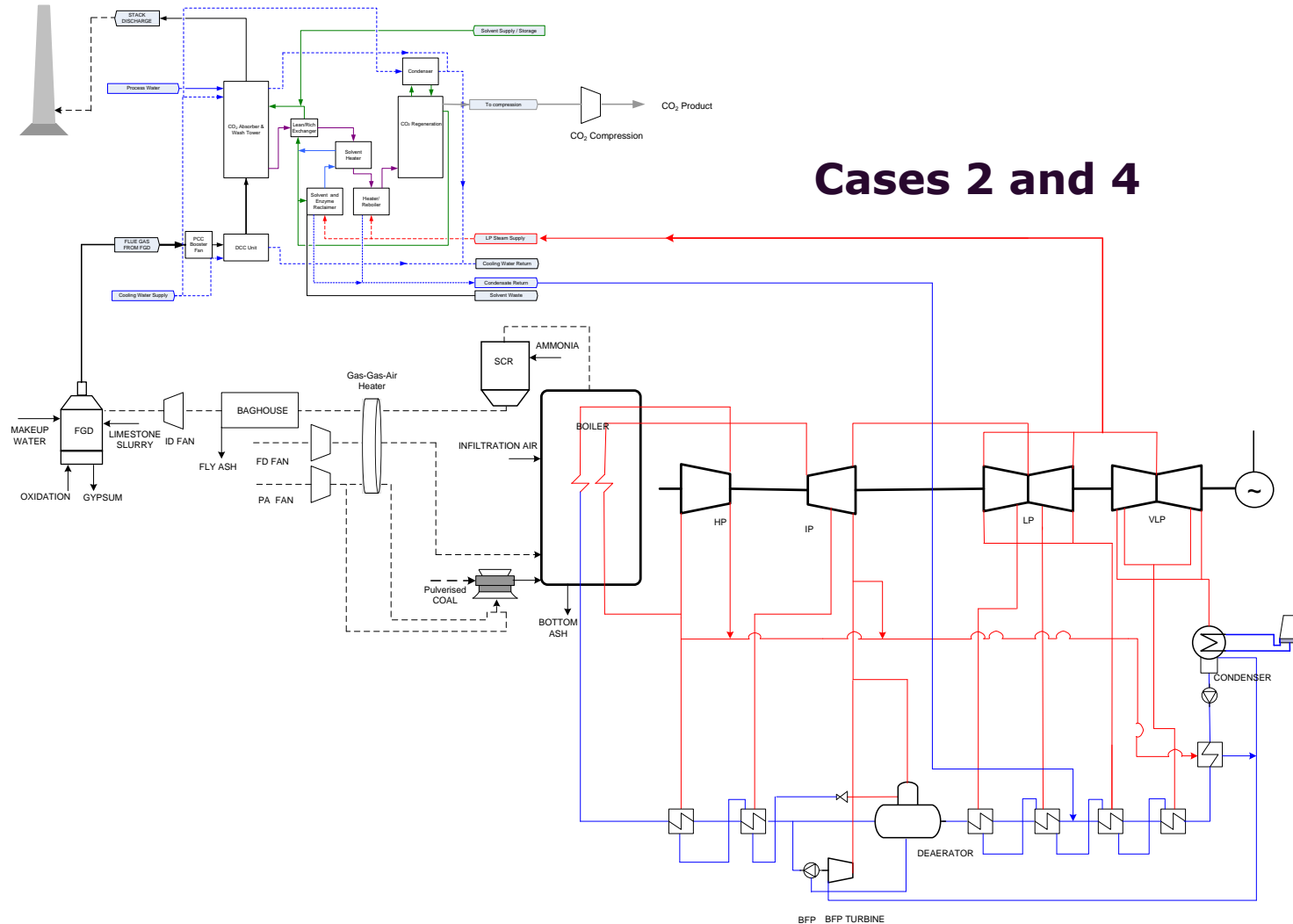
Simplified Process Flow Diagram of PCC Plant



BFD for Subcritical PC Power Plant with PCC



BFD for Subcritical PC Power Plant with Optimized PCC cases



Specific Energy Requirements and Power Summary

Utilizing an electrical power equivalent of 0.0911 kWh/lb

	NETL_2007 Case 10	Case 1	Case 2	Case 3	Case 4
GROSS (STEAM TURBINE) POWER, kWe	679,923	702,321	826,695	861,695	843,695
CO ₂ Capture System Auxiliaries	23,500	27,798	27,798	27,798	27,798
Vapor Compression	N/A	30,459	30,459	791	791
Ultrasonic Energy Demand	N/A	N/A	N/A	138,469	15,000
Total Auxiliaries, kWe	130,310	165,067	165,067	273,868	150,399
NET POWER, kWe	549,613	537,254	661,628	587,827	693,296
Net Plant Efficiency (HHV)	24.90%	24.34%	29.97%	26.63%	31.41%
Net Plant Heat Rate (Btu/kWh)	13,724	14,040	11,401	12,832	10,880
CO ₂ Regeneration Energy (kg of CO ₂ /kWh _e)	3.445	3.299	9.566	4.497	18.531
% Improvement over Case 10	-	- 4.25	177.68	30.52	437.91

Specific Energy Requirements and Power Summary

Utilizing an electrical power equivalent of 0.0665 kWh/lb

	NETL_2007 Case 10	Case 1	Case 2	Case 3	Case 4
GROSS (STEAM TURBINE) POWER, kWe	679,923	696,274	777,616	812,616	794,616
CO ₂ Capture System Auxiliaries	23,500	27,798	27,798	27,798	27,798
Vapor Compression	N/A	30,459	30,459	791	791
Ultrasonic Energy Demand	N/A	N/A	N/A	138,469	15,000
Total Auxiliaries, kWe	130,310	165,067	165,067	273,868	150,399
NET POWER, kWe	549,613	531,207	612,549	538,749	644,217
Net Plant Efficiency (HHV)	24.90%	24.07%	27.75%	24.41%	29.19%
Net Plant Heat Rate (Btu/kWh)	13,724	14,200	12,314	14,001	11,709
CO ₂ Regeneration Energy (kg of CO ₂ /kWh _e)	4.719	4.266	9.566	4.497	18.531
% Improvement over Case 10	-	-9.613	102.71	-4.72	292.68

PCC Plant Capital Cost Breakdown

Total Post Combustion Capture Plant Cost details (Millions of 2007\$)								
	Equip	Labor	Mats./ Consum.	Bare Erect. Cost	Eng., CM & Fee Cost	Contingencies		Total Plant Cost,MM\$
						Process	Project	
Vacuum Regeneration – Cases 1 and 2	229.82	54.95	9.21	293.98	39.16	58.80	73.49	465.44
Ultrasonic Regeneration – Cases 3 and 4	211.76	52.04	8.32	272.11	37.95	54.42	68.03	432.51
Case 10	214.99	65.21	-	280.19	26.59	56.04	72.57	435.39

- Contingencies utilized for all the cases
 - 20% - Process Contingency
 - 25% - Project Contingency

LCOE for Options Considered

Utilizing an electrical power equivalent of 0.0911 kWh/lb

Summary of Levelized Costs (2007 \$/MWh _e)	NETL_2007 Case 9	NETL_2007 Case 10	Case 1	Case 2	Case 3	Case 4
Fuel Cost	20.43	30.06	30.75	24.97	28.11	23.83
Capital Cost	34.44	68.71	70.51	67.72	67.37	65.80
Variable Operating Cost	5.88	10.92	13.94	11.32	12.51	10.61
Fixed Operating Cost	3.89	5.86	5.99	4.867	5.47	4.64
Transportation, Sequestration & Monitoring	-	4.04	4.04	4.04	4.04	4.04
Total	64.64	119.59	125.23	112.92	117.50	108.92
Increase versus No Capture	-	85.04%	93.78%	74.72%	81.79%	68.51%

- The best case was Case 4 with a 68.51% LCOE increase compared with Case 9.
- This can be further reduced by
 - Validation of the technology by bench-scale testing
 - Lower contingencies with increased confidence in the technology
 - Lower capital cost by using alternative methods and materials for construction
 - Lower operating cost by reducing enzyme utilization (make-up and dosing)

LCOE for Options Considered

Utilizing an electrical power equivalent of 0.0665 kWh/lb

Summary of Levelized Costs (2007 \$/MWh _e)	NETL_2007 Case 9	NETL_2007 Case 10	Case 1	Case 2	Case 3	Case 4
Fuel Cost	20.43	30.06	30.79	26.70	30.36	25.39
Capital Cost	34.44	68.71	70.03	68.37	68.27	66.25
Variable Operating Cost	5.88	10.92	13.94	11.32	12.51	10.61
Fixed Operating Cost	3.89	5.86	6.00	5.21	5.91	4.94
Transportation, Sequestration & Monitoring	-	4.04	4.04	4.04	4.04	4.04
Total	64.64	119.59	126.06	117.56	123.29	113.02
Increase versus No Capture	-	85.04%	95.03%	81.89%	90.75%	74.86%

- The lowest LCOE increase was for Case 4 compared with Case 9.
- This can be further reduced by
 - Validation of the technology by bench-scale testing
 - Lower contingencies with increased confidence in the technology
 - Lower capital cost by using alternative methods and materials for construction
 - Lower operating cost by reducing enzyme utilization (make-up and dosing)

Sensitivity Analysis

Sub-cases considered based on Case 4:

Case 4a: Dosing of Enzyme reduced by an order of magnitude

Case 4b: 50% reduced enzyme activity loss with dosing as in Case 4a

Case 4c: 50% decreased Ultrasonic Energy demand for regeneration.

Case 4d: 50% reduction in Ultrasonic regeneration section's capital cost.

	Case 4	Case 4a	Case 4b	Case 4c	Case 4d
LCOE (\$/MWh_e)	108.91	106.39	106.25	108.7	107.9
% increase	68.5%	64.6%	64.4%	68.3%	67.0%

Conclusions and Recommendations

- Preliminary techno-economic evaluation has been completed for novel enzyme-activated potassium carbonate PCC process using ultrasonically-enhanced regeneration integrated with a subcritical coal-fired power plant.
- Net Plant Efficiency (on HHV basis) and LCOE (\$/MWh_e):

		Net efficiency	LCOE (\$/MWh _e)
	Case 10	24.9%	119.6
Power Equivalent of 0.0911 Kwh/lb of steam	Vacuum Regeneration	24.34% – 29.97%	112.92 – 125.23
	Ultrasonic Regeneration	26.63% – 31.41%	108.90 – 117.50
Power Equivalent of 0.0665 Kwh/lb of steam	Vacuum Regeneration	24.07% - 27.75%	117.56 – 126.06
	Ultrasonic Regeneration	24.41% - 29.19%	113.02 – 123.29

- Challenges that will be investigated in the next phases of the project are:
 - Validation and optimization of the performance, design of the ultrasonic regeneration
 - Optimization of the dosing quantity of the enzyme and reduction in thermal degradation.
 - Detailed Investigation of the option to utilize a VLP for solvent regeneration steam extraction at 8psia (and 85 °C).
 - Utilization of alternative materials of construction to reduce the capital cost of plant, such as the use of concrete columns, plastic packing materials etc.

Plans for Bench-scale Evaluation

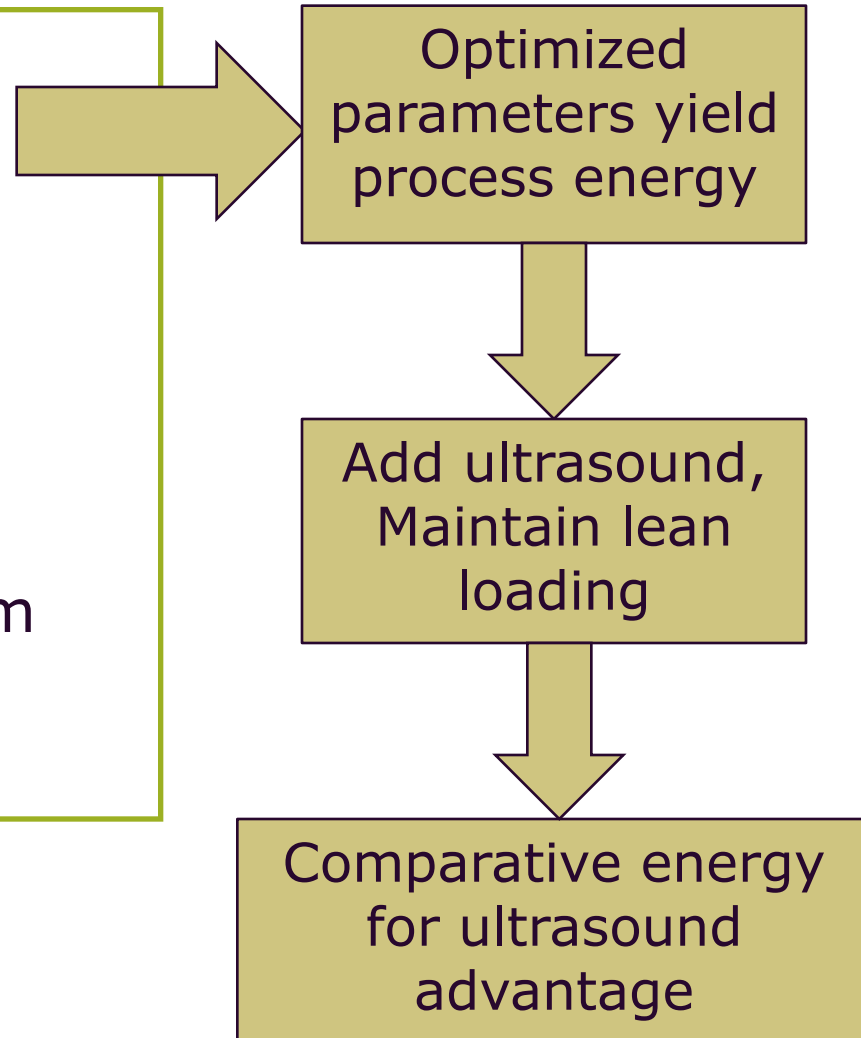


Plans for Bench-scale Evaluation

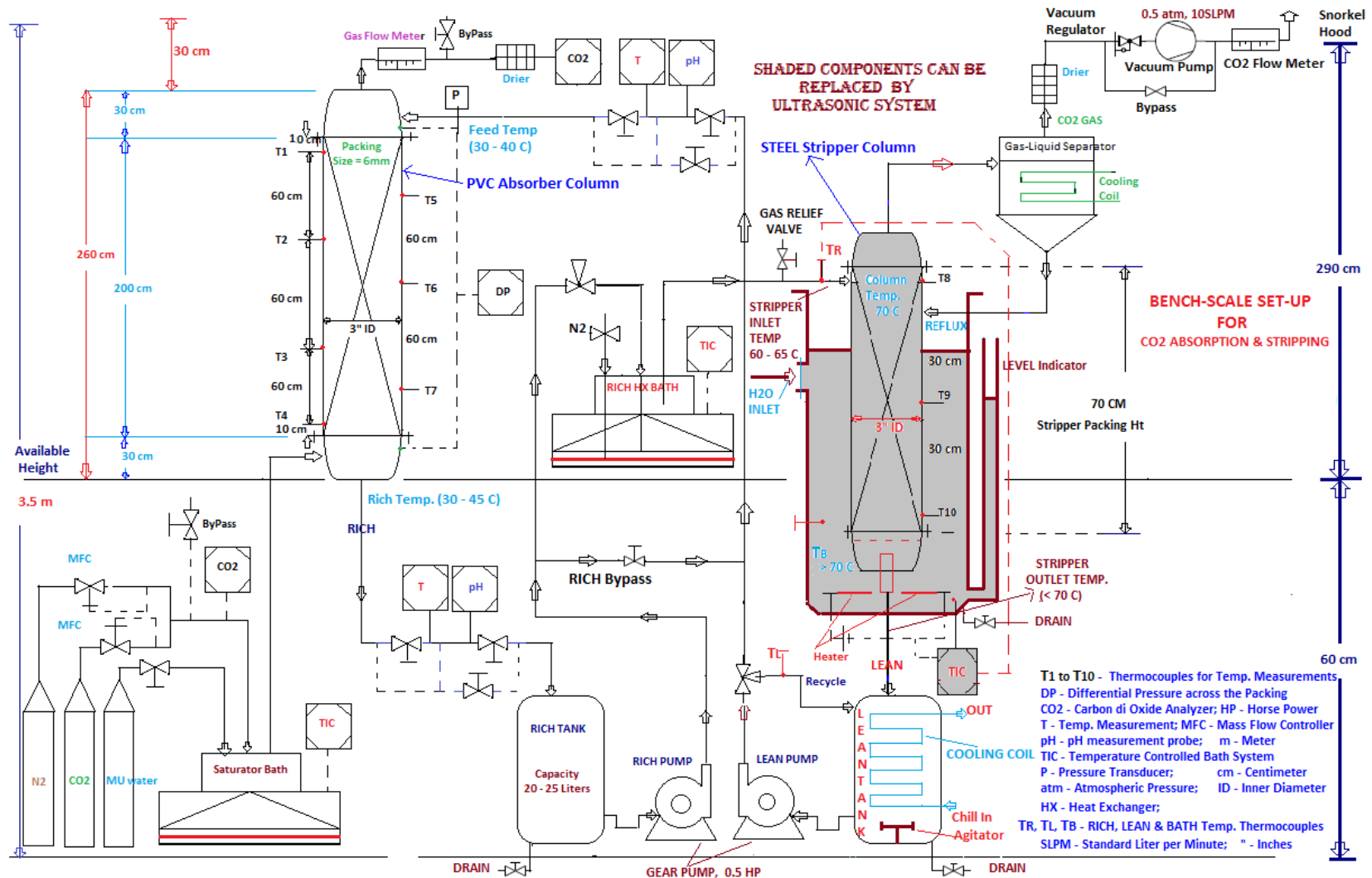
Task No.	Description	Resp. (Lead)	End
4	Bench Unit Procurement & Fabrication		4/13
4.1	Absorber procurement and fabrication	K	2/13
4.2	Regenerator procurement and fabrication	P	4/13
4.3	Host Rig procurement and fabrication	K	2/13
4.4	Enzyme supply for bench-scale testing	N	2/13
5	Unit Operations Shake-down Testing		9/13
5.1	Absorber testing (vac regen)	K	7/13
5.2	Regenerator testing (ultrasonic regen)	P	6/13
5.3	Long-term enzyme stability testing	N	9/13
5.4	Integrate units to bench-scale system	K	9/13
6	Bench-scale Testing	K	9/14
7	Full Technology Assessment	D	12/14

Key Bench-scale Operational Parameters

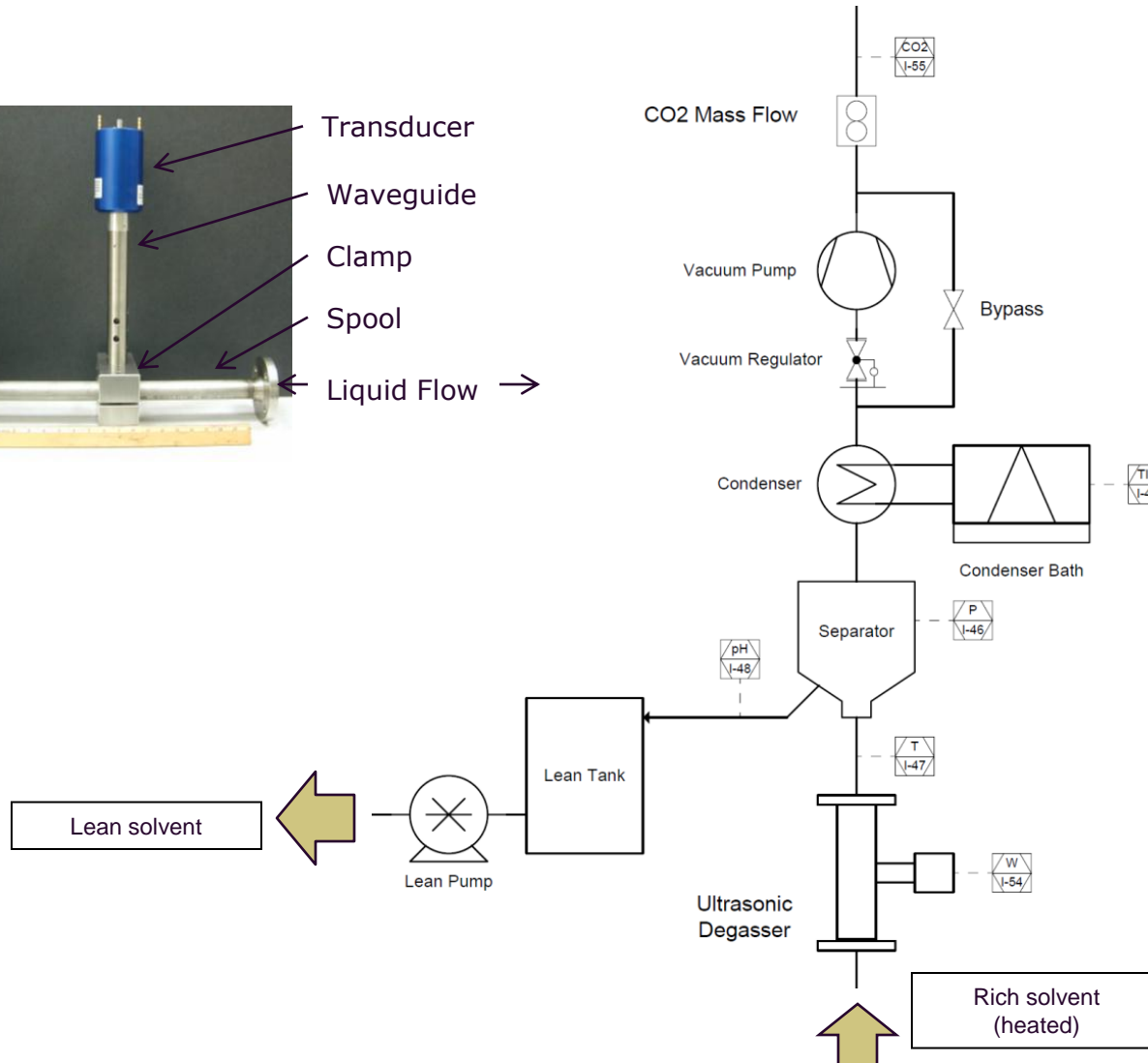
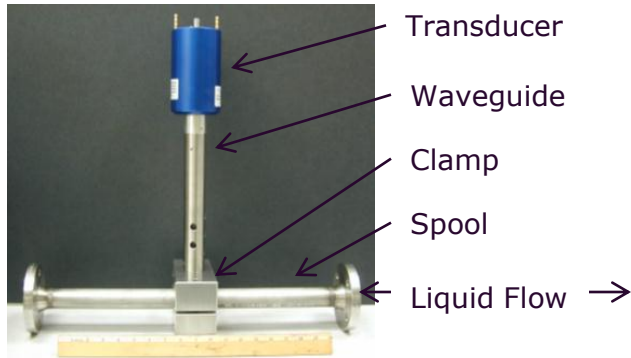
- Flow rates
 - Gas: 10- 30 SLPM
 - Liquid : 100-300 ml/min
- Liquid temperature
 - Absorber inlet: 30-40 °C
 - Stripper outlet: 70-80 °C
- Stripper pressure: 0.25-0.4 atm
- Enzyme dose: 3-5 g/L



Bench-scale Design



Ultrasonic Regenerator Unit for Bench-scale



Bench-scale Test Matrix: Build & Shakedown

Location	Main Task Item	Expected Results
UK-CAER	Fabrication of Absorber and Vacuum Stripper Unit	Unit ready for preliminary experiments
UK-CAER	Preliminary Experiments	Loading and flooding point, flooding and pressure drop correlation
UK-CAER	Mass Transfer Experiments with K ₂ CO ₃ w/ CA Enzyme	Demonstrate absorber performance and optimum condition
UK-CAER	Desorption by Vacuum Stripping	Comparative case for ultrasonic stripping
PNNL	Fabrication and Shakedown of Ultrasonic Stripper Unit	Ultrasonic setup ready for bench-scale experiments
PNNL	Additional Equipment Sizing in a Flowing Configuration	Confirmation of design parameters based on initial data in a flowing condition
PNNL	Procurement, Assembly and Shakedown of Bench-Scale Equipment	Confirmation of equipment performance prior to bench-scale testing

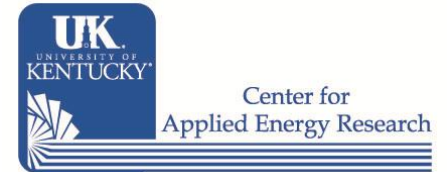
Bench-scale Test Matrix: Integrated Operation

Location	Main Task Item	Expected Results
UK-CAER (& PNNL)	Integration of Pre-tested Ultrasonic Regenerator Unit with Absorber	Operable integrated system
UK-CAER	Shakedown Testing of Integrated Bench Scale Unit	EH&S met and fully functional integrated system
UK-CAER	Parametric Testing	Optimized ultrasonic stripping
UK-CAER	500 Hours of Integrated Testing	Performance data set for use in final techno-economic feasibility
NZ	Enzyme Longevity Testing by Bench System Monitoring	Updated longevity expectations for dosing program and solvent reclamation assumptions

Enzyme Test Matrix: Performance Validation

Location	Main Task Item	Expected Results
NZ	Enzyme Robustness Testing – Batch Lab Analyses Mimicing Bench-scale Conditions	More rigorously defined limits of enzyme performance
NZ	Enzyme Dosing Reduction	Reduce enzyme dose required for adequate performance in bench-scale testing
NZ	Evaluate desorption enhancement with enzyme at 70°C	Inform impact on desorption
NZ	Lab-scale evaluation of “cook and filter” solvent reclamation approach	Inform efficacy of approach

Conclusions & Recommendations



Main Messages

Key Findings

- Within the boundaries of the pre-feasibility framework, the concept could provide 25% reduction in LCOE versus Case 10, with a potential to reduce to 51%
- An integrated design for bench-scale has been established
- Lab results support moving to bench-scale testing

Path Forward

- Project team recommends proceeding to BP2 (as soon as possible)
- Technical gaps identified in BP1 that are important for bench-scale testing are incorporated in the go-forward plan
- Certain technical and commercial aspects will need to be addressed outside the scope of this project

Opportunities Beyond Current Project Scope

- Optimal ultrasonic spool design
 - Current project utilizes equipment currently available from commercial vendors
 - Advanced configurations would likely offer better performance and lower cost
- Improved enzyme candidate
 - Kinetic performance
 - Longevity in working solvent
 - Requires dedicated screening and protein engineering



Thank You

Acknowledgements

DOE-NETL

Andrew Jones

PNNL

Charles Freeman (PM)
Kayte Denslow, Richard Zheng, Mark Bearden

UK-CAER

Joe Remias (PM)
Balraj Ambedkar

DPS

Vinay Mulgundmath (PM)
Saravanan Swaminathan, Agnieszka
Kuczyńska, Scott Hume

NZ

Sonja Salmon (PI/PM)
Alan House, Megan Beckner Whitener